Masterarbeit

What is the potential of zero free charge and potential of zero total charge? Electrochemical studies of the electrical double layer in the presence and absence of specific adsorption

Self-assembled monolayers (SAMs) prepared by adsorption on a solid surface of species dissolved in the electrolyte solution provide a convenient and flexible method to tailor the interfacial properties of solid supports. Since the discovery if disulfide adsorption on the Au surface by Nuzzo and Allara in 1983, SAMs of alkanethiols and their derivatives have been widely used in many fields of research, which includes electrochemistry, molecular electronics, biomimetics and nanomaterials. Obviously, the chemisorption of thiol molecules on the Au electrode surface changes the composition and thus charge density and capacitance of the electrical double adjacent to the unmodified and thiol modified gold electrode.

The potential of zero charge is a fundamental property of the metal|electrolyte interface, whose knowledge is critical for a detailed understanding of the double layer phenomenon. However, the adsorption of organic species on the electrode surface may lead to a large (more than 1 V) negative or positive shift of the potential of zero charge. When the electrode is covered by a thiol monolayer, the charge density σ_M of the Au electrode is a function of the electrode potential (E) and the surface Gibbs excess (Γ) of the monolayer: $\sigma_M = f(\Gamma, E)$. One can distinguish two values of the potential of zero charge. The first is measured at a constant surface concentration of the thiol in the monolayer on the Au surface. In this case, the surface coverage is constant and the charging of the interface by altering the electrode potential involves only a change in the free charge density, which is responsible for the development of the electrochemical double layer at the interface. The potential at which the free charge is equal to zero is referred as potential of zero free charge. The second value of the zero charge is measured by so celled “reductive desorption” method, where the voltage is stepped between the adsorption and desorption potentials. The charge measured in this reductive desorption method is called the total charge and includes both the charge flowing from the electrode to change the oxidation state of thiol molecules and the charging of the electrical double layer. The potential at which the total charge is equal to zero is referred as potential of the zero total charge.

In this work monolayers of 6-mercaptohexanol and thiol derivatives of DNA will be prepared on the Au electrode surface. Potential of zero free charge and zero total charge will be determined using electrochemistry. In this study cyclic voltammetry, chronocoulometry and alternative current voltammetry will be used to determine both charge and capacitance of the Au|electrolyte interface. In order to discuss the impact of the electrolyte composition and specific adsorption of anions on the Au surface electrolyte solution will contain phosphate, nitrate and perchlorate ions. The impact of the specific adsorption of anions on the Au surface on the values of the two potential of zero charge will be investigated and discussed.

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